

Electrochemical characterization of novel layered Cu_2MS_4 materials for Li-ion batteries (M = Mo)



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ABSTRACT

Electrochemical performance of Cu_2MoS_4 was evaluated. When the cutoff potential is limited between 1.6 and 3.0 V, the material can give stable cycle performance of up to 100 mA h g^{-1} . However, the material shows slow kinetics within this region. The material can give a discharge capacity of up to 653 mA h g^{-1} when discharged to 0.6 V vs. Li/Li^+ , with a first cycle efficiency of 61.3%. This corresponds to an insertion of 8.5 Li and an extraction of 5.2 Li from the material. XRD and XPS measurements both suggest Cu displacement from the material during discharge and charge, which is a possible reason for the poor cycle stability of the material. A reaction mechanism is proposed based on the XPS analysis. Better cycle performance is observed for $\text{Cu}_2\text{MoS}_4/\text{GO}$ composite.

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1. Introduction

Metal sulfides were previously studied as cathode materials in Li-ion batteries back in the 1980s [1]. It was found that Li ions could be intercalated and de-intercalated into layered metal sulfides such as TiS_2 and MoS_2 , with a mechanism similar to that of layered oxide such as LiCoO_2 . Initial usage of these materials was to combine them with Li metal or lithiated Al as the anode to form a lithium battery. However, because the lithium battery with metal sulfides has low capacity and low voltage, researches on cathode materials have been shifted mainly to layered oxide materials since then. Recently, there have been renewed interests to use metal sulfides as anode materials instead because they can undergo conversion and/or alloying reactions at lower voltages, resulting in high capacities [2–13]. Metal sulfides however have their disadvantages, namely high reaction potential with respect to Li/Li^+ (i.e. low overall battery voltage) and also the dissolution of polysulfide from the material into the electrolyte during charge and discharge. Among the different metal sulfides, MoS_2 and WS_2 have attracted much attention recently because they have a layered structure that may be used in applications such as energy storage, transistors, etc. [14]. As anodes for lithium ion

batteries, a reversible capacity of $>900 \text{ mA h g}^{-1}$ was previously reports on MoS_2 -graphene composite [11], MoS_2 nanoplate [10] and MoS_x on multiwall carbon nanotubes [15] between 0 and 3.0 V vs. Li/Li^+ . After first cycle, the main reduction and oxidation peaks of MoS_2 is observed by cyclic voltammetry to be around 2.0 and 2.3 V, respectively. MoS_3 , another form of molybdenum sulfide, was shown to have an initial capacity of 372 mA h g^{-1} between 1.0 and 3.0 V with reduction and oxidation peaks at 1.7 and 2.4 V [4], slightly different from that of MoS_2 when tested with the same scan rate. This suggests that even with the same type of elements in a compound, reaction mechanism may differ depending on the material structure and composition. It would therefore be possible to tune the electrochemical performance by changing the structure and composition of the sulfide material.

We have synthesized a new class of layered metal sulfides with the formula of Cu_2MS_4 (where M = Mo or W) based on previous works [16–18]. These materials were demonstrated previously as electrocatalyst for hydrogen production [19]. The material has a tetragonal structure, which is different from that of MoS_2 and MoS_3 . We have therefore evaluated the materials for battery applications to understand how the electrochemical behavior can change with structure and composition. The multi-valence of Mo and W together with the possibility of a conversion reaction with S will give high capacities. The role of Cu in the material can also be crucial to the performance of the material [2]. Previous works on

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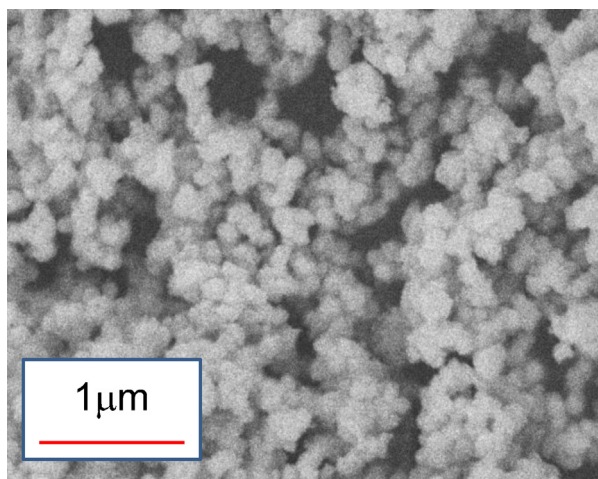


Fig. 1. Scanning electron microscopy of Cu_2MoS_4 .

Table 1
Theoretical capacities of Cu_2MS_4 .

Reaction	No. of e^- transfer	M = Mo (mA h g^{-1})	M = W (mA h g^{-1})
$\text{Cu}_2\text{MS}_4 \rightarrow \text{Li}_2\text{Cu}_2\text{MS}_4$	2	152	122
$\text{Cu}_2\text{MS}_4 \rightarrow \text{Li}_4\text{MS}_4 + 2\text{Cu}$	4	305	244
$\text{Cu}_2\text{MS}_4 \rightarrow 4\text{Li}_2\text{S} + 2\text{Cu} + \text{M}$	8	610	488

intercalation into molybdenum cluster sulfides $\text{M}_x\text{Mo}_6\text{S}_8$ (Chevrel phases such as $\text{Cu}_4\text{Mo}_6\text{S}_8$) were carried out [20,21] but the layered Cu_2MS_4 materials potentially offer higher capacity. Table 1 shows the theoretical capacity of Cu_2MS_4 assuming different reactions. Mo and W were found to be at an oxidation state of 6+ for the as-synthesized material [19]. If two electrons can be inserted into the material, a capacity of 152 and 122 mA h g^{-1} can be obtained for Mo and W, respectively. If a copper displacement reaction occurs, the number of electrodes transferred will be doubled. Further reduction of the transition metal to metallic state will give up to eight electrons transfer. In this study, the electrochemical performance of Cu_2MoS_4 with different cutoff potential was first evaluated. The kinetics of the oxidation–reduction reaction at high potential was studied by cyclic voltammetry. Finally, the charge–discharge mechanism of the material was elucidated by X-ray diffraction (XRD) and X-ray photoemission spectroscopy (XPS).

2. Experimental

2.1. Material synthesis and characterization

Layered Cu_2MoS_4 is synthesized through a wet chemistry using $(\text{NH}_4)_2\text{MoS}_4$ and $\text{Cu}(\text{CH}_3\text{CN})\text{BF}_4$ [19]. The precursors were dissolved in dimethylformamide (DMF) and acetonitrile and reflux at 135 °C for 1 day in N_2 atmosphere. The resulting powder is filtered and dried. Cu_2MoS_4 with 10% graphene oxide ($\text{Cu}_2\text{MoS}_4/\text{GO}$) is also synthesized for comparison. Graphene oxide was first synthesized by modified Hummer's method, a typical method used by other researchers [22]. Graphene oxide is added into the DMF/acetonitrile solution prior to reflux.

Structure of the materials was studied by X-ray diffraction (XRD) with a $\text{Cu K}\alpha$ source (Bruker). To investigate the change in structure after electrochemical tests, cells were discharged to different states of discharge and were disassembled in an Ar glove box. The electrodes were washed with dimethyl carbonate (DMC), and put into a sealed PMMA holder from Bruker in the Ar glove box before taking out for measurements. This precaution was used to prevent reaction between the charged electrode with water and oxygen in the atmosphere.

Ex-situ X-ray photoemission spectroscopy (XPS) measurements were also carried out on electrodes at different states of discharged to monitor the local environment of Li, Cu and Mo in the material.

Morphology and particle size of the tested materials were studied by scanning electron microscopy (SEM). Surface area of the material is obtained by the Brunauer–Emmett–Teller method (BET).

2.2. Electrochemical evaluation

The active material was mixed with acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 6:2:2. The materials were mixed in 1-methyl-2-pyrrolidone (NMP) to form a slurry. The slurry is then coated on roughened aluminum foil as a current collector using a doctor blade. Al foil is used so that the Cu from the material can be distinguished from the current collector during spectroscopies. The electrode was then dried at 80 °C and pressed in a roll press. The electrodes were cut into 16 mm diameter discs and dried again at 110 °C in vacuum before assembling with Li metal as counter electrodes in a 2016 coin cell. 1 M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC) to diethyl carbonate (DEC) of 1:1 is the typical electrolyte used in the cell.

The cells were then tested with a battery tester between 0.6 to 3.0 V vs. Li/Li^+ . Because of the usage of Al current collector for the

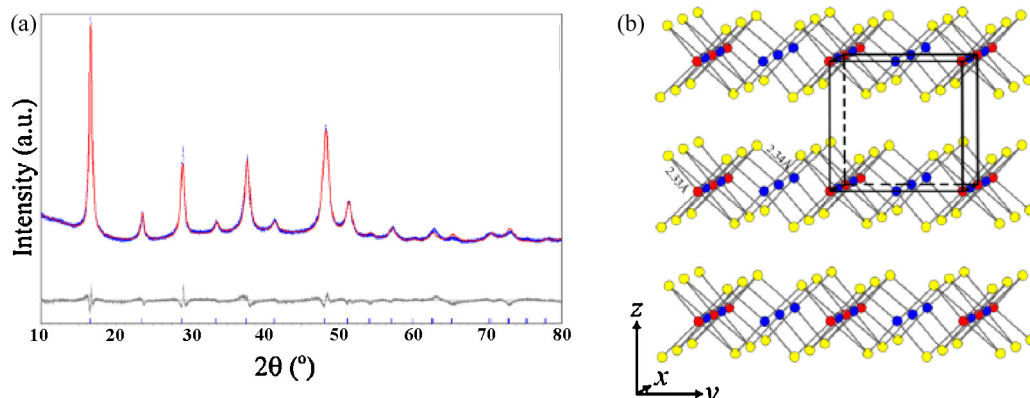


Fig. 2. (a) XRD of the as-synthesized Cu_2MoS_4 ; (b) tetragonal structure of Cu_2MoS_4 .

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